TITLE: Kinetics of Fly Ash Beneficiation by Carbon Burnout

Technical Report

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Kinetics of Beneficiated Fly Ash by Carbon Burnout

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ABSTRACT

The presence of carbon in fly ash requires an increase in the dosage of the air-entraining admixture for concrete mix, and may cause the admixture to lose efficiency. Specifying authorities for the concrete producers have set maximum allowable levels of residual carbon. These levels are the so called "Loss On Ignition" (LOI). The concrete producers' day-to-day purchasing decisions sets the LOI at 4%. The objective of the project is to investigate the kinetics of oxidation of residual carbon present in coal fly ash as a possible first step toward producing low-carbon fly ash from high-carbon, low quality fly ash.

INTRODUCTION

Coal fly ash is gaining increased use as a substitute in concrete products. Typical specifications state that fly ash may be used to replace up to 15% of the cement, [1]. Some recent work, [1- 3], indicate that much higher volume application of fly ash is possible. From a concrete producer's standpoint, the only important characteristics of fly ash are those that have the ability to influence concrete properties, [4, 5]. The mechanism by which fly ash creates a discontinuous pore structure and clogs pore channels with additional hydration products are well known, [6]. The reactions slow transport rates for both water and chlorides through the cementitious paste. Consumption of water-soluble calcium hydroxide (produced as a by-product in the hydration of Portland cement) by the pozzolanic reaction creates additional calcium silicate gel, which is much denser than the gel without pozzolan. Increases in fly ash usage as a percentage of total cementitious material enhance the described property. Reduction of the calcium hydroxide content of the concrete and decreased permeability as a result of the pozzolanic reaction also contribute to the sulfate resistance of fly ash-containing concrete. Sulfate attack on concrete results in the formation of gypsum compounds and ettringite with subsequent increase in solid volume in the cement matrix, and expansion, [7,8]. Use of Class F fly ash in concrete mix reduces the absolute amount of calcium aluminate available to support ettringite formation which effectively reduces the cement content. In terms of freezing and thawing resistance, a Bureau of Reclamation study [4], has shown that the use of either Class F or Class C fly ash produces concrete with resistance to freeze-thaw cycles more superior to Portland cement concrete of equivalent strength, [9]. As coal fly ash gains increased use in concrete mix much attention is being paid to the residual carbon content. In general, most bituminous coal will produce fly ash meeting specifications governing chemical makeup and pozzolanic activity. The presence of carbon requires an increase in the dosage of the air-entraining admixture, and may cause the admixture to lose efficiency. Specifying authorities have set maximum allowable levels of residual carbon. These levels are the so called "Loss On Ignition" (LOI). The concrete producers' day-to-day purchasing decisions sets the LOI at 4%. The objective of the project is to investigate the kinetics of oxidation of residual carbon present in coal fly ash as a possible first step toward producing low-carbon fly ash from high-carbon, low quality fly ash.

THEORETICAL BACKGROUND

The reaction of carbon with oxidizing gases are well documented and known to be controlled by the following processes, [10 - 12].

- Mass transfer of gaseous reactants from the bulk gas phase to the carbon surface.
- Adsorption of reactants on the surface
- Chemical reaction on the surface mobility and formation of adsorbed products
- Desorption of products
- Mass transport (by diffusion) of gaseous products away from the carbon surface

If the temperature is well controlled, the diffusion of reactant gas from and away from the carbon surface can usually be ignored. At low temperatures then the reaction is chemically controlled and the true activation energy of the reaction can be determined. The adsorption process may be considered as molecular involving an atom or a molecule from the gas phase and an active carbon atom on the carbon surface. The activation energy required may be used to form an activated complex between the molecule or atom and the active carbon atom. Desorption from an immobile layer involves an activated state in which a molecule attached to an adsorbing center acquires the proper configuration and activation energy to permit it to escape from that surface. The reaction rate R in terms of mass loss is given by

$$R = -\frac{dm}{dt} = k_{air} \Sigma(O) P^n \quad (1)$$

where k_{air} is the reaction rate coefficient, P is the pressure of the reacting gas, n is the reaction order and $\Sigma(O)$ the surface area. This equation is based on the rate law proposed by Hinshelwood, [11]:

$$R = -\frac{dm}{dt} = k_{air} \Sigma(O) \frac{P^n}{1 + k' P^n_{CO} + k'' P^n_{CO_2}} \quad (2)$$

for the reaction between a porous solid and gas. Equation (2) reverts to equation (1) if

$$1 \gg k' P^n_{CO} + k'' P^n_{CO_2} \quad (3)$$

The temperature dependence of carbon gasification is evaluated from the Arrhenius equation:

$$k = Ae^{-(E_a/RT)} \quad (4)$$

where k is the rate constant, R is the universal gas constant and T is the absolute reaction temperature. The corresponding values of activation energy and the frequency factor A are also calculated with the aid of the above equations. The absolute rate theory is used to obtain the frequency factor from the equation:

$$AN_o = \frac{k_B T}{h} \frac{f^*}{f} \quad (5)$$

Where N_o is Avogadro's number, k_B is Boltzmann's constant, T is the absolute temperature, h

is Planck's constant, and f^* and f_a are the partition functions of the transition state complex and the absorbed species, respectively, [12].

Combustion occurs when fuel, oxygen and heat are combined. Residual carbon in fly ash is the source of fuel, the reactant gas - air is the source of oxygen and temperatures of 550 °C and above are known to sustain autoignition. The absence of any one of the above three components will prevent occurrence of combustion. The reaction kinetics are governed by the degree to which each component is present. Thus by controlling the fuel, the oxygen and temperature at which the reaction is allowed to occur, it is possible to control the reaction rate. This approach is used in the present studies.

EXPERIMENTAL

sample preparation

The coal fly ash samples (type F), employed in this study was supplied by Delmarva Power Company and came from their Indian River (Delaware), power plant. The samples were first dried at 200 °C under nitrogen for 3 hours using a Lindberg furnace. Subsequently they were fractioned into various particle size groups using sieve sizes 5,10,45,75 and 125 μm . All dried samples were kept in airtight desiccators at all times.

Surface Area Measurement

A Micromeritics model 2000 accelerated surface area porosimeter (ASAP), was used to study the N_2 adsorption isotherms (77 K) of the dried powdered samples. Approximately 45 to 50 mg of sample was evacuated at 250 °C for about 24 hours under dynamic vacuum of about 10^{-4} torr. After cooling, the samples were kept in a N_2 atmosphere and later evacuated with a drag pump. The porosity characteristics were obtained from the various reduction methods contained in the apparatus software: Brunauer Emmel & Teller (BET), Harkins & Jura (HJ), Horwarth & Kawazoe (HK) and Density Functional Theory (DFT) methods.

Reaction Rates

The reactivity in air of carbon in the fly ash were measured in a Cahn Thermogravimetric Analyzer (TGA) in the temperature range 550 °C - 750 °C for three particle sizes. The TGA balance was sensitive to 0.1 μg and the furnace was capable of temperatures up to 1100 °C. The reaction chamber was purged with helium for 30 min before the temperature was raised to the desired reaction temperature. At the selected temperature the reaction rate was determined at three partial pressures, 1.0, 0.8, and 0.6 atm. Approximately 50 mg of sample was placed inside the TGA furnace. The temperature was raised at a controlled heating rate, 20 - 25 °C min^{-1} , under nitrogen flow until it reached the preset final oxidation temperature. Once the set temperature had been attained the N_2 gas flow was discontinued. The reaction was initiated by introducing a high purity, dried air at a controlled flow of 60 cc/s. The samples remained in the furnace for 1 - 4

hours as they cooled to room temperature under the air flow. The air temperature, sample weight and the time derivative of the weight loss were continuously recorded. For runs at different oxygen partial pressures, vacuum was applied to the chamber during the isotherm period of the run.

RESULTS AND DISCUSSION

Surface Area Data

Figure 1 shows the isotherm obtained for sample #100 at 77 K. The BJH adsorption/desorption report following each run indicated that there were no open pores at either end. Thus it seems reasonable to interpret this as a confirmation that the carbon burnoff reaction is in the zone II kinetic control regime, [10,13]. In Figure 2 is a typical pore volume distribution with respect to pore radius obtained for each of the specimen analyzed. The characteristic shows that there exist at least five size range exist in the fly ash samples; micropores with pore radius between 10 and 50 Å. The porosity of the fly ash samples used in this study appear to depend on their carbon content. The BET surface area data are shown in Table 1.

Property	#100	#200	#325
Pore Size	nm	nm	nm
r_{avg} (2V/A by BET)	2.234	2.239	2.491
d_{avg} (Adsorption)	5.788	5.809	5.758
d_{avg} (Desorption)	5.117	4.459	4.994
Surface Area	m ² /g	m ² /g	m ² /g
S_{BET}	5.535	3.992	3.002
S_{BJH} (adsorption)	2.623	2.214	1.836
Volume	cm ³ /g	cm ³ /g	cm ³ /g
V_{BJH} (adsorption)	0.0076	0.0064	0.0053

Table 1. Pore size, surface area and volume data of unreacted fly ash by N₂ adsorption/desorption at 77 K. BJH Adsorption/Desorption report showed no open pores at either ends.

The average adsorption pore diameter is about the same for all the three sample cuts. The

adsorption surface areas on the other hand decreases with increasing sieve size which is to be expected as the large sieve number represents a smaller particle diameter and carbon content.

Reaction Rates

Oxidation reactions were carried out on three different size-fractionated samples at temperature of 550 , 650 and 750 °C respectively. At each temperature, the reaction was carried out at a reactant gas pressure of 0.213 atm, 0.168 atm and 0.126 atm. Thus a total of twenty seven runs were carried out for nine oxidation reactions. The reaction rates were calculated for each oxidation reaction using both the initial rates and the proportionality law. A typical weight loss-time characteristics is shown in figure 3 for the fly ash sample #100. The initial rate law [12], employs the linear portion of the sigmoid curve of the weight loss v time. Thus in figure 3 the data before the point indicated by the arrow are considered suitable for computing the initial rate. The proportionality law , [14] , considers the entire reaction and employs the slope of the line obtained therefrom. In figures 4 and 5 the pressure dependence of the reaction rates are shown for the initial rates and proportionality law respectively for the three temperature settings for sample #100. Linear regressions in figures 4 and 5 gave values of slopes within 98% confidence levels. In either case the rate of reaction was normalized to the initial weight and surface area of the particular size fraction. Tables 2 through 4 show the reaction rates obtained at three partial pressures (0.213, 0.168 and 0.126 atm) of oxygen for the three sample size cuts respectively.

Temp °C	Rate mg/g.m ² .sec		Rate mg/g.m ² .sec		Rate mg/g.m ² .sec	
	0.213 atm		0.168 atm		0.126 atm	
	Ri	Rp	Ri	Rp	Ri	Rp
550	0.0188	2.267	0.0302	3.182	0.0345	3.533
650	0.0736	12.165	0.1036	19.787	0.1710	23.908
750	0.1520	28.630	0.1830	121.462	0.2320	123.012

Table 2. Rate dependence on temperature for three different partial pressures of O₂ for fly ash sieved at #100.

Temp °C	Rate mg/g.m ² .sec		Rate mg/g.m ² .sec		Rate mg/g.m ² .sec	

	0.213 atm		0.168 atm		0.126 atm	
	Ri	Rp	Ri	Rp	Ri	Rp
550	0.0069	7.306	0.0100	3.953	0.0147	37.093
650	0.0219	165.032	0.0213	59.323	0.1100	19.099
750	0.1586	618.738	0.1629	320.759	0.1724	143.103

Table 3. Rate dependence on temperature for three different partial pressures of O_2 for fly ash sieved at #200.

Temp °C	Rate mg/g.m ² .sec		Rate mg/g.m ² .sec		Rate mg/g.m ² .sec	
	0.213 atm		0.168 atm		0.126 atm	
	Ri	Rp	Ri	Rp	Ri	Rp
550	0.0035	12.098	0.0265	7.757	0.0675	60.793
650	0.0290	72.420	0.1296	79.421	0.2110	343.650
750	0.1462	548.638	0.2252	504.078	0.2455	828.588

Table 4. Rate dependence on temperature for three different partial pressures of O_2 for fly ash sieved at #325.

As expected the reaction rate shows an increase with increasing temperature under the same pressure of oxygen for all the sample pack. The "i" and "p" shown in brackets are meant to represent the reaction rates calculated from initial rate and proportionality law respectively. In all cases, the reaction rates obtained with the proportionality law were higher than those obtained with the initial rate law. Activation energies were computed from the slope of the graph of the Arrhenius plots ($\log k$ v $1/T$) The values obtained are shown in Table 5.

Pres. (O_2) Atm.	Sieve # 100	Sieve #200	Sieve #325
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	Activation Energy (Ea) , kJ/mole					
	Ea(i)	Ea(p)	Ea(i)	Ea(p)	Ea(i)	Ea(p)
0.213	73.85	89.67	108.40	157.43	131.44	135.06
0.168	63.81	127.23	95.78	154.91	76.12	146.43
0.126	68.28	124.37	88.07	--	43.92	92.37

Table 5. Activation Energies for oxidation reaction of fly ash at three partial pressures of O₂
 Ea(i) : initial rate law; Ea(p) : proportionality law

The values are consistent with those obtained by Milligan and Altwicker, in their catalytic gasification of carbon in incinerator fly ash, [15]. The data also show that the reaction rate effect of temperature varied with particles size. The sample cut #100 shows a relatively constant value for Ea over the range of reactant gas pressures. Thus effect of mass transport on activation energy is negligible for this case. For the sample packs #200 and #325 on the other hand, do show pronounced mass transport effect on the activation energy. At O₂ pressure of 0.213 atm the activation energy for #325 fly ash is 131.44 kJ/mole. As the pressure decreases so does the activation energy and at 0.126 atm it is a mere 43.92 kJ/mole. The surface area analyses of the unreacted fly ash indicate that the samples were porous with the porosity depending on the amount of carbonaceous matter, [16-18]. It reasonable, therefore to suggest that mass transport effects may have played a role. For porous materials, the concentration of reactant gas decreases to almost zero inside the pores at low partial pressures of the reactant gas, thereby lessening the effect of increasing temperatures on the reaction rate. This is consistent with the expectation that oxygen molecules cannot enter micropores fast enough at low temperatures, [13]. As already mentioned, the carbon burnoff reaction is in the zone II kinetic regime.

Conclusion

The rate dependence of oxidation of fly ash on partial pressure of O₂ shows a trend of

decreasing rate with total pressure for both initial rates and rates calculated from the proportionality law. The effect of temperature on the rate varied with particle size although the activation energy showed a somewhat steady value over the range of reactant gas pressures employed for the larger #100 fly ash. Mass transport effects appears to significant for some sample pack only. Future studies will be directed at exploring the full range of sizes for which the effect is significant.

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Fig 3. Time derivative weight loss of the fly ash at a pressure (O_2) of 0.213 atm.

s#100 at 750 C

Initial Rates

s#100 at 650 C

ln R vs. ln P

s#100 at 550 C

ln R vs. ln P

Fig 4. Rate dependence on Pressure (Initial rates)

Proportionality Law

s#100 at 750 C

s#100 at 650 C

s#100 at 550 C

Fig 5. Rate dependence on Pressure (Proportionality Law)